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Serial No. 10/088,265 : Group Art Unit 1615  
Filed March 18, 2002 : Examiner P. Short

POLYORTHOESTER AND CURABLE  
COMPOSITION CONTAINING THE SAME

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**DECLARATION**

Commissioner for Patents  
P. O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Akiko KOJIMA, declare and say:

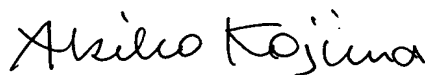
that I am thoroughly conversant in both the Japanese and English languages;

that I am presently engaged as a translator in these languages;

that the attached document represents a true English translation of the  
Japanese Priority Application No. 263820/99, filed September 17, 1999.

I further declare that all statements made herein of my own knowledge are true  
and that all statements made on information and belief are believed to be true; and  
further that these statements were made with the knowledge that willful false  
statements and the like so made are punishable by fine or imprisonment, or both,  
under Section 1001 of Title 18 of the United States Code, and that such willful false  
statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 10th day of May, 2004.



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Akiko KOJIMA



(TRANSLATION)

PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following  
application as filed with this Office.

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Application Number: Patent Application No. 263820/99

Applicant(s) : Kansai Paint Co., Ltd.

October 13, 2000

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Kozo OIKAWA

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Commissioner,  
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[Name of Object] Specification

[Name of Object] Abstract 1  
[Proofing] Required

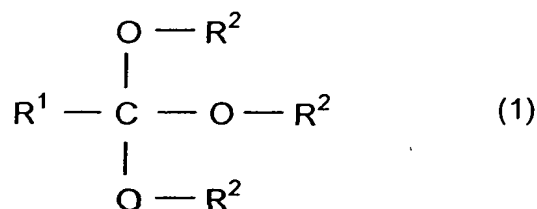
[Document Name] Specification

[Title of the Invention] Polyorthoester and Production Process for the Same

[Claims]

[Claim 1] A polyorthoester prepared by reacting:

- 5 (A) an orthoester represented by the following Formula (1):



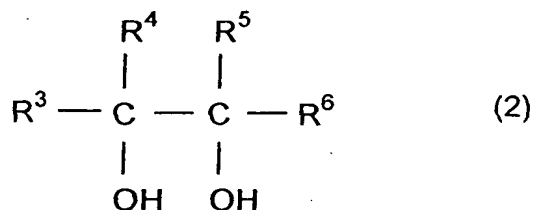
- 10 wherein  $\text{R}^1$  represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and three  $\text{R}^2$ 's may be the same or different and each represent an alkyl group having 1 to 4 carbon atoms,

(B) at least one glycol compound selected from  $\alpha$ -glycols and  $\beta$ -glycols, and

- 15 (C) a hydroxyl group-containing compound having at least two hydroxyl groups in a molecule other than the compound (B) set forth above.

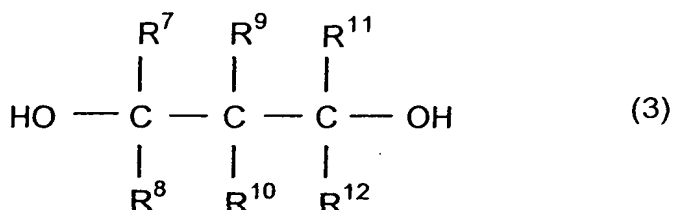
[Claim 2] The polyorthoester as set forth in Claim 1, wherein the orthoester (A) is at least one compound selected from methyl orthoformate, ethyl orthoformate, methyl orthoacetate and ethyl orthoacetate.

- 20 [Claim 3] The polyorthoester as set forth in Claim 1 or 2, wherein the glycol compound (B) is at least one glycol compound selected from an  $\alpha$ -glycol represented by the following Formula (2):



- 25 wherein  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  may be the same or different and each represent a

hydrogen atom, an alkyl group having 1 to 24 carbon atoms, an aralkyl group having 7 to 24 carbon atoms or a phenyl group, or a group obtained by substituting a part of these groups with an oxygen atom, and the total of the carbon atoms in the groups represented by  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  falls in a range of 0 to 24; and  $R^4$  and  $R^5$  may form a cyclic structure together with carbon atoms to which they are bonded directly, and a  $\beta$ -glycol represented by the following Formula (3):



10

wherein  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  and  $R^{12}$  may be the same or different and each represent a hydrogen atom, an alkyl group having 1 to 24 carbon atoms, an aralkyl group having 7 to 24 carbon atoms or a phenyl group, or a group obtained by substituting a part of these groups with an oxygen atom, and the total of the carbon atoms in the groups represented by  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  and  $R^{12}$  falls in a range of 0 to 24; and  $R^7$  and  $R^9$  or  $R^7$ ,  $R^9$  and  $R^{11}$  may form a cyclic structure together with carbon atoms to which they are bonded directly.

[Claim 4] The polyorthoester as set forth in any one of Claims 1 to 3, wherein the glycol compound (B) is at least one compound selected from ethylene glycol, 1,2-propylene glycol, 1,2-hexanediol, neopentyl glycol, 2-methyl-1,3-propanediol, 2-methyl-2,4-pentanediol, 3-methyl-1,3-butanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol and 2-butyl-2-ethyl-1,3-propanediol.

[Claim 5] The polyorthoester as set forth in any one of Claims 1 to 4, wherein the hydroxyl group-containing compound (C) has a molecular weight falling in a range of 90 to 100,000 and a hydroxyl group value falling in a range of 20 to 1,850.

[Claim 6] The polyorthoester as set forth in any one of Claims 1 to 5, wherein a hydroxyl group contained in the hydroxyl group-containing compound (C) is

blocked by an orthoester of a 5-membered ring or a 6-membered ring constituted by the orthoester (A) and the glycol compound (B).

[Claim 7] A production process for a polyorthoester characterized by subjecting the orthoester (A), the glycol compound (B) and the hydroxyl group-containing compound (C) each set forth in Claim 1 to condensation reaction in the presence of an acid catalyst.

[Claim 8] The process as set forth in Claim 7, wherein the orthoester (A) in a proportion falling in a range of 0.05 to 5 moles is reacted with the glycol compound (B) in a proportion falling in a range of 0.05 to 5 moles each per equivalent of a hydroxyl group contained in the hydroxyl group-containing compound (C).

[Detailed Description of the Invention]

[0001]

[Technical field to which the invention belongs]

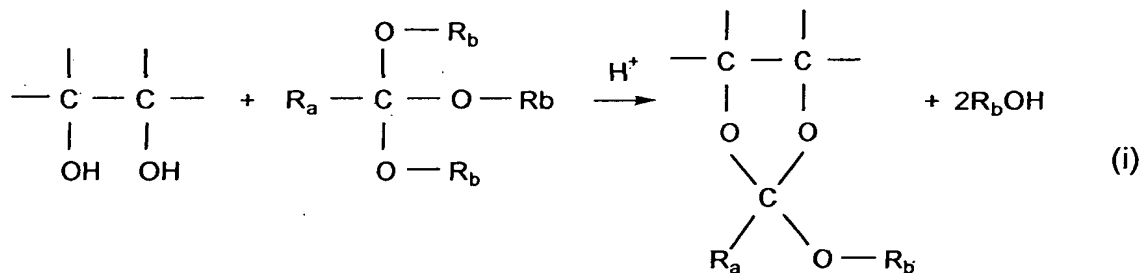
The present invention relates to a polyorthoester and a production process for the same, more specifically to a novel polyorthoester which has a low viscosity and is readily controlled in a molecular weight and which has a high degree of freedom in molecular design, and a production process for the same.

[0002]

[Prior art and its problem]

An orthoester has so far been used as a dehydrating agent and a synthetic raw material for various compounds. Further, an orthoester is known as a protective group for a hydroxyl group and protects a hydroxyl group on such moderate conditions as a room temperature in the presence of an acid catalyst by reaction as shown in the following Equation (i):

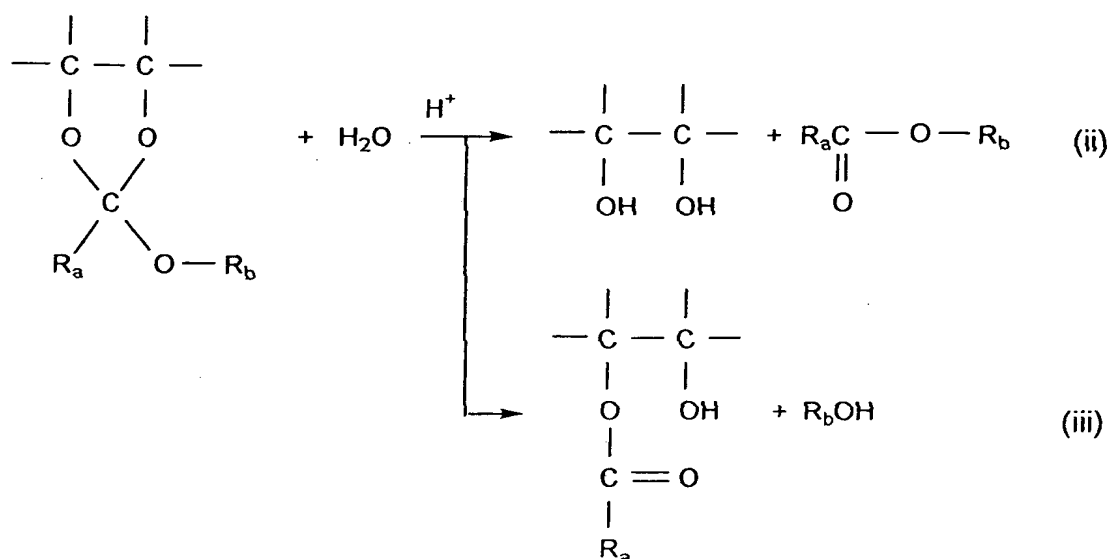
[0003]



[0004]

The protected hydroxyl group is stable under a base condition, but the protective group is readily desorbed under an acid condition by hydrolysis as shown in the following Equation (ii) or (iii):

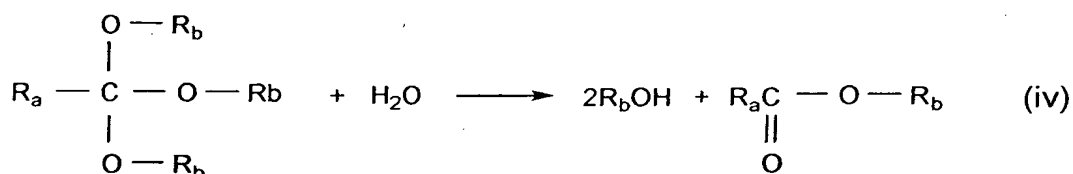
5 [0005]



[0006]

In general, an orthoester is easily hydrolyzed to form two molecules of alcohol and one molecule of ester:

10 [0007]



[0008]

Proposed are several techniques on a polyorthoester industrially making use of such characteristics of the polyorthoester. For example, a polyorthoester for a photoresist is described in Japanese Patent Publication No.20325/1988, and a polyorthoester for drug delivery is described in Japanese Patent Application Laid-Open No.502465/1993.

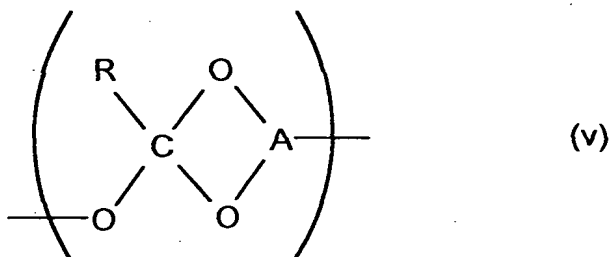
[0009]

The polyorthoesters described in these official gazettes are



compounds which are obtained by condensing triols with orthoesters and which have a specific repetitive unit, for example, a repetitive unit represented by the following Formula (v). However, in producing this compound, only specific triol can be used as a hydroxy group-containing compound, and it has a degree of a freedom only in such an extent that a molecular weight can be changed by a blending ratio of the triol to the orthoester, so that there is the problem that a degree of freedom in molecular design is low.

[0010]



10 [0011]

Further, a polymer having a spiroorthoester structure is described in Japanese Patent Application Laid-Open No.42724/1982, and it is shown that the above polymer is a cross-linking high polymer having a small volumetric shrinkage. However, caprolactone is essentially used as a raw material, and therefore, a degree of freedom in molecular design is low. Furthermore, a polymer having a bicycloorthoester structure is described in Japanese Patent Application Laid-Open No.233114/1985, and it is shown that the above polymer is a cross-linking high polymer having an excellent balance between an elastic modulus and a toughness. However, trimethylolpropane or trimethylolethane is essentially used as a raw material, and therefore, involved therein is the problem that a degree of freedom in molecular design is low.

[0012]

It is known, as described above, that an alkoxy group of an orthoester is subjected to alcohol exchange reaction with a hydroxyl group in the presence of an acid catalyst, and a 5-membered ring, a 6-membered ring or a bicyclo ring can be formed by using a hydroxyl group-containing compound in which two hydroxyl groups are close. Making use of this property, an orthoester is used as a protective group for close hydroxyl groups mainly in the

biochemical field.

[0013]

Three alkoxy groups of an orthoester can be subjected to alcohol exchange reaction, and it can be turned into a polyorthoester by combining with polyhydric alcohol. In this case, if an orthoester is subjected merely to exchange reaction with polyhydric alcohol (condensation reaction by dealcohol), it is gelatinized by converting into three dimension.

[0014]

One object of the present invention is to provide a novel polyorthoester having a high degree of freedom in molecular design and a low viscosity and capable of being readily controlled in a molecular weight.

[0015]

The other object of the present invention is to provide an industrially useful process in which capable of being easily produced is a novel polyorthoester having a low viscosity and capable of being readily controlled in a molecular weight.

[0016]

[Means to solve the problems]

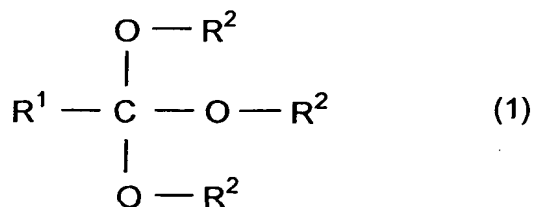
The present inventors repeated intensive investigations in order to solve the above problems. As a result, they found that the above problems could be solved by reacting a specific glycol compound, an orthoester and a polyhydric hydroxyl group-containing compound to prepare a polyorthoester, and they have come to complete the present invention.

[0017]

That is, the present invention provides a polyorthoester prepared by reacting:

(A) an orthoester represented by the following Formula (1):

[0018]



[0019]

wherein R<sup>1</sup> represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and three R<sup>2</sup>'s may be the same or different and each represent an alkyl group having 1 to 4 carbon atoms,

5 (B) at least one glycol compound selected from α-glycols and β-glycols, and

(C) a hydroxyl group-containing compound having at least two hydroxyl groups in a molecule other than the compound (B) described above.

[0020]

10 Further, the present invention provides a production process for a polyorthoester characterized by subjecting the orthoester (A), the glycol compound (B) and the hydroxyl group-containing compound (C) each described above to condensation reaction in the presence of an acid catalyst.

[0021]

15 The present invention shall be explained below in further details.

[0022]

[Mode for carrying out the invention]

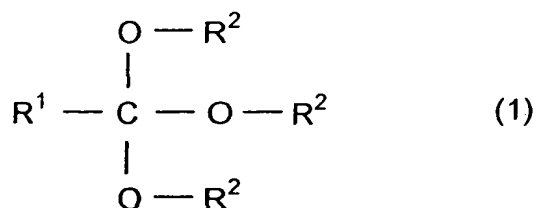
The polyorthoester of the present invention is a reaction product of the orthoester (A), the glycol compound (B) and the hydroxyl group-containing  
20 compound (C) each described below.

[0023]

Orthoester (A):

The orthoester which is the component (A) is a compound represented by the following Formula (1):

25 [0024]



[0025]

wherein R<sup>1</sup> represents a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and three R<sup>2</sup>'s may be the same or different and each represent an alkyl

group having 1 to 4 carbon atoms.

[0026]

In Formula (1) described above, the alkyl group having 1 to 4 carbon atoms represented by  $R^1$  or  $R^2$  is linear or branched and includes, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl and t-butyl.

[0027]

The specific examples of the orthoester (A) include, for example, methyl orthoformate, ethyl orthoformate, propyl orthoformate, butyl orthoformate, methyl orthoacetate, ethyl orthoacetate, methyl orthopropionate, ethyl orthopropionate, methyl orthobutyrate and ethyl orthobutyrate. Among them, methyl orthoformate, ethyl orthoformate, methyl orthoacetate and ethyl orthoacetate are suited. They may be used alone or in combination of two or more kinds thereof.

[0028]

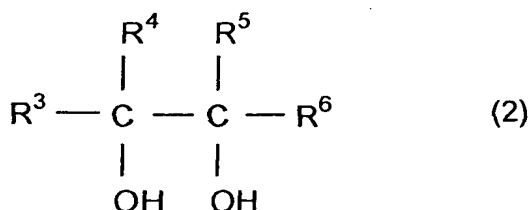
15 Glycol compound (B):

The glycol compound which is the component (B) is at least one glycol compound selected from  $\alpha$ -glycols and  $\beta$ -glycols having two hydroxyl groups in a molecule.

[0029]

20 Among them, a compound represented by the following Formula (2) can suitably be used as the  $\alpha$ -glycol:

[0030]



[0031]

25 wherein  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  may be the same or different and each represent a hydrogen atom, an alkyl group having 1 to 24 carbon atoms, an aralkyl group having 7 to 24 carbon atoms or a phenyl group, or a group obtained by substituting a part of these groups with an oxygen atom, and the total of the carbon atoms in the groups represented by  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  falls in a range of

0 to 24, preferably 0 to 10; and  $R^4$  and  $R^5$  may form a cyclic structure together with carbon atoms to which they are bonded directly.

[0032]

In Formula (2) described above, the alkyl group having 1 to 24  
5 carbon atoms represented by  $R^3$ ,  $R^4$ ,  $R^5$  or  $R^6$  is linear, branched or cyclic and includes methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, pentyl, hexyl, n-octyl, 2-ethylhexyl, decyl, dodecyl, octadecyl, cyclohexyl, methylcyclohexyl, cyclohexylmethyl and cyclohexylethyl.

[0033]

10 In Formula (2) described above, the aralkyl group having 7 to 24 carbon atoms represented by  $R^3$ ,  $R^4$ ,  $R^5$  or  $R^6$  is preferably an alkyl group substituted with phenyl, and the specific examples thereof include benzyl and phenethyl.

[0034]

15 In Formula (2) described above, the group obtained by substituting a part of the alkyl group, the aralkyl group or the phenyl group with an oxygen atom represented by  $R^3$ ,  $R^4$ ,  $R^5$  or  $R^6$  includes, for example, an alkoxyalkyl group such as methoxymethyl, ethoxymethyl, propoxymethyl and butoxymethyl; an alkanoyloxyalkyl group such as acetoxymethyl and acetoxyethyl; and an  
20 aryloxyalkyl group such as phenoxyethyl and phenoxyethyl.

[0035]

Among them,  $R^3$ ,  $R^4$ ,  $R^5$  or  $R^6$  in Formula (2) described above is preferably a hydrogen atom or an alkyl group having 1 to 6 carbon atoms.

[0036]

25 In Formula (2) described above, the cyclic structure which can be formed by  $R^4$  and  $R^5$  together with carbon atoms to which they are bonded directly includes, for example, a cyclohexyl group and a cyclopentyl group.

[0037]

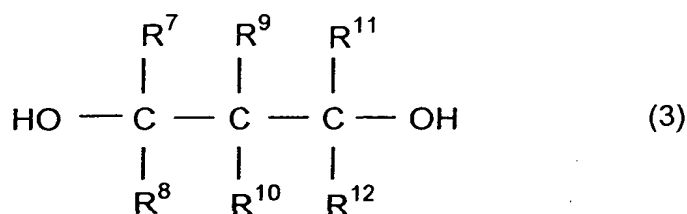
Thus, the representative examples of the  $\alpha$ -glycols include, for  
30 example, ethylene glycol, 1,2-propylene glycol, 1,2-butylene glycol, 2,3-butylene glycol, 1,2-hexanediol, 1,2-dihydroxycyclohexane, pinacol and hydrolysis products of long chain alkyl monoepoxides; fatty acid monoglycerides ( $\alpha$  products) such as glycerin monoacetate ( $\alpha$  product) and glycerin monostearate

( $\alpha$  product); and 3-ethoxypropane-1,2-diol and 3-phenoxypropane-1,2-diol. Among them, ethylene glycol, 1,2-propylene glycol and 1,2-hexanediol are suited.

[0038]

- 5 On the other hand, particularly a compound represented by the following Formula (3) can suitably be used as the  $\beta$ -glycol:

[0039]



[0040]

- 10 wherein  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  and  $R^{12}$  may be the same or different and each represent a hydrogen atom, an alkyl group having 1 to 24 carbon atoms, an aralkyl group having 7 to 24 carbon atoms or a phenyl group, or a group obtained by substituting a part of these groups with an oxygen atom, and the total of the carbon atoms in the groups represented by  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  and  
15  $R^{12}$  falls in a range of 0 to 24; and  $R^7$  and  $R^9$  or  $R^7$ ,  $R^9$  and  $R^{11}$  may form a cyclic structure together with carbon atoms to which they are bonded directly.

[0041]

- In Formula (3) described above, the alkyl group having 1 to 24 carbon atoms represented by  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  or  $R^{12}$  includes the same ones  
20 as those described above as the alkyl group represented by  $R^3$ ,  $R^4$ ,  $R^5$  or  $R^6$  in Formula (2) described above.

[0042]

- In Formula (3) described above, the aralkyl group having 7 to 24 carbon atoms represented by  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  or  $R^{12}$  is preferably an alkyl  
25 group substituted with phenyl, and the specific examples thereof include benzyl and phenethyl.

[0043]

In Formula (3) described above, the group obtained by substituting a part of the alkyl group, the aralkyl group or the phenyl group with an oxygen

atom represented by  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  or  $R^{12}$  includes, for example, an alkoxyalkyl group such as methoxymethyl, ethoxymethyl, propoxymethyl and butoxymethyl; an alkanoyloxyalkyl group such as acetoxymethyl and acetoxylethyl; and an aryloxyalkyl group such as phenoxymethyl and phenoxyethyl.

[0044]

In Formula (3) described above, the cyclic structure which can be formed by  $R^7$  and  $R^9$  or  $R^7$ ,  $R^9$  and  $R^{11}$  together with carbon atoms to which they are bonded directly includes, for example, a cyclohexyl group and a cyclopentyl group.

[0045]

Among them,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $R^{11}$  or  $R^{12}$  in Formula (3) described above is preferably a hydrogen atom or an alkyl group having 1 to 6 carbon atoms.

[0046]

Thus, the representative examples of the  $\beta$ -glycols include, for example, neopentyl glycol, 2-methyl-1,3-propanediol, 2-methyl-2,4-pentanediol, 3-methyl-1,3-butanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-phenoxypropane-1,3-diol, 2-methyl-2-phenylpropane-1,3-diol, 1,3-propylene glycol, 1,3-butylene glycol, dimethylolpropionic acid, dimethylolbutanoic acid, 2-ethyl-1,3-octanediol and 1,3-dihydroxycyclohexane; and fatty acid monoglycerides ( $\beta$  products) such as glycerin monoacetate ( $\beta$  product) and glycerin monostearate ( $\beta$  product). Among them, suited are neopentyl glycol, 2-methyl-1,3-propanediol, 2-methyl-2,4-pentanediol, 3-methyl-1,3-butanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,2,4-trimethyl-1,3-pentanediol and 2-butyl-2-ethyl-1,3-propanediol.

[0047]

(C) Hydroxyl group-containing compound:

The hydroxyl group-containing compound which is the component (C) is a compound having two or more hydroxyl groups in a molecule other than the glycol compound (B) described above.

[0048]

The hydroxyl group-containing compound (C) includes compounds having two hydroxyl groups other than  $\alpha$ -glycols and  $\beta$ -glycols, or compounds having 3 or more hydroxyl groups in a molecule.

[0049]

5           The compounds having two hydroxyl groups other than  $\alpha$ -glycols and  $\beta$ -glycols include, for example, 1,4-butanediol, 1,4-dihydroxycyclohexane, 1,5-pentanediol, 1,6-hexanediol, 2,5-hexanediol, 3-methyl-1,5-pentanediol, 1,4-dimethylolcyclohexane, tricyclodecanedimethanol, 2,2-dimethyl-3-hydroxypropyl-2,2-dimethyl-3-hydroxypropionate (this compound  
10 corresponds to ester of hydroxypivalic acid and neopentyl glycol), bisphenol A, bisphenol F, bis(4-hydroxyhexyl)-2,2-propane, bis(4-hydroxyhexyl)methane, 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5,5]undecane, diethylene glycol, triethylene glycol, tetra- or more polyethylene glycol, dipropylene glycol, tripropylene glycol, tetra- or more polypropylene glycol,  
15 copolymers having hydroxyl groups at both terminals obtained by copolymerizing ethylene oxide with propylene oxide, linear polyesters having hydroxyl groups at both terminals such as polycaprolactonediol, polycarbonatediol and carboxylic acid adducts of diepoxide.

[0050]

20           The compounds described above having 3 or more hydroxyl groups include, for example, glycerin, diglycerin, triglycerin, pentaerythritol, dipentaerythritol, sorbitol, mannitol, trimethylolethane, trimethylolpropane, ditrimethylolpropane, tris(2-hydroxyethyl)isocyanurate, gluconic acid and polymers having 3 or more hydroxyl groups (polyesters, polyethers, acryl  
25 polymers, ketone resins, phenol resins, epoxy resins, urethane resins those having 3 or more hydroxyl groups; polyvinyl alcohols which are saponified products of polyvinyl acetates; and natural saccharides such as glucose).

[0051]

30           Capable of being suitably used as the hydroxyl group-containing compound (C) are the compounds having a hydroxyl group value falling in a range of 20 to 1,850 mg KOH/g, particularly 40 to 1,650 mg KOH/g.

Production of polyorthoester:

In producing the polyorthoester of the present invention, a blending



ratio of the orthoester (A), the glycol compound (B) and the hydroxyl group-containing compound (C) shall not specifically be restricted. In general, it is suitable, in terms of an easiness in controlling the molecular weight, to use the orthoester (A) in a proportion falling in a range of 0.01 to 10 moles, preferably 0.05 to 5 moles and more preferably 0.1 to 2 moles; and the glycol compound (B) in a proportion falling in a range of 0.01 to 10 moles, preferably 0.05 to 5 moles and more preferably 0.1 to 2 moles, each per equivalent of a hydroxyl group contained in the hydroxyl group-containing compound (C).

[0052]

10           The polyorthoester of the present invention can be obtained by subjecting the three components (A), (B) and (C) described above to condensation reaction. For example, it can suitably be produced by heating the three components described above at a temperature falling in a range of usually a room temperature to 250°C, preferably 70 to 200°C for approximately 15   1 to 20 hours, if necessary, in the presence of an organic solvent and an acid catalyst to subject them to condensation reaction.

[0053]

          In the present invention, an alkoxy group of the orthoester (A) causes exchange reaction with the alcohol parts of the glycol compound (B) and the hydroxyl group-containing compound (C). In this case, the orthoester (A) is 20   preferentially reacted with the  $\alpha$ -glycol or  $\beta$ -glycol which is the glycol compound (B) having hydroxyl groups close to each other to form a cyclic structure. That is, the glycol compound (B) is cyclized by preferentially reacting with two functional groups (alkoxyl groups) of the orthoester (A) which is trifunctional.

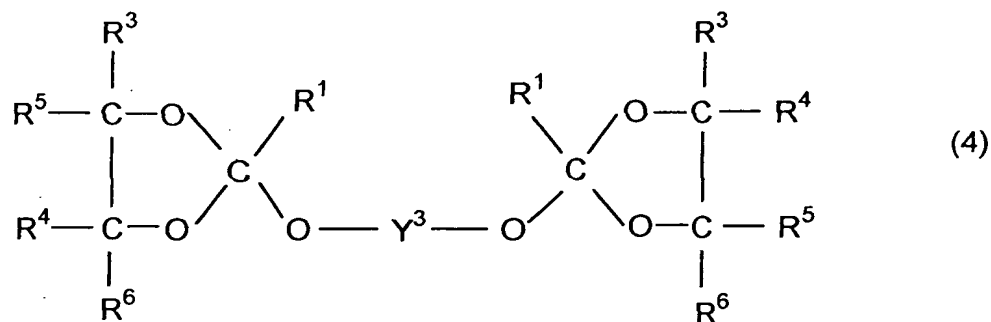
25   The remaining one alkoxyl group of the orthoester is reacted with the hydroxyl group-containing compound (C). Thus, cross-linking between the molecules is not brought about in producing the polyorthoester of the present invention, and therefore, the resulting polyorthoester can be inhibited from being increased in a molecular weight and a viscosity. On the other hand, if the orthoester (A) is 30   reacted directly with the hydroxyl group-containing compound (C) in the absence of the glycol compound (B), cross-linking between the molecules takes place, so that the product is rapidly increased in a molecular weight and a viscosity. The present invention has made it possible to inhibit the product

from being increased in a molecular weight and a viscosity to control them by further adding the glycol compound (B) to the orthoester (A) and the hydroxyl group-containing compound (C) to react them.

[0054]

- 5 When used as the raw materials are, for example, the orthoester represented by Formula (1) described above, the  $\alpha$ -glycol represented by Formula (2) described above and the compound having 2 hydroxyl groups in a molecule, the polyorthoester of the present invention produced in the manner described above can have a structure represented by the following Formula (4):

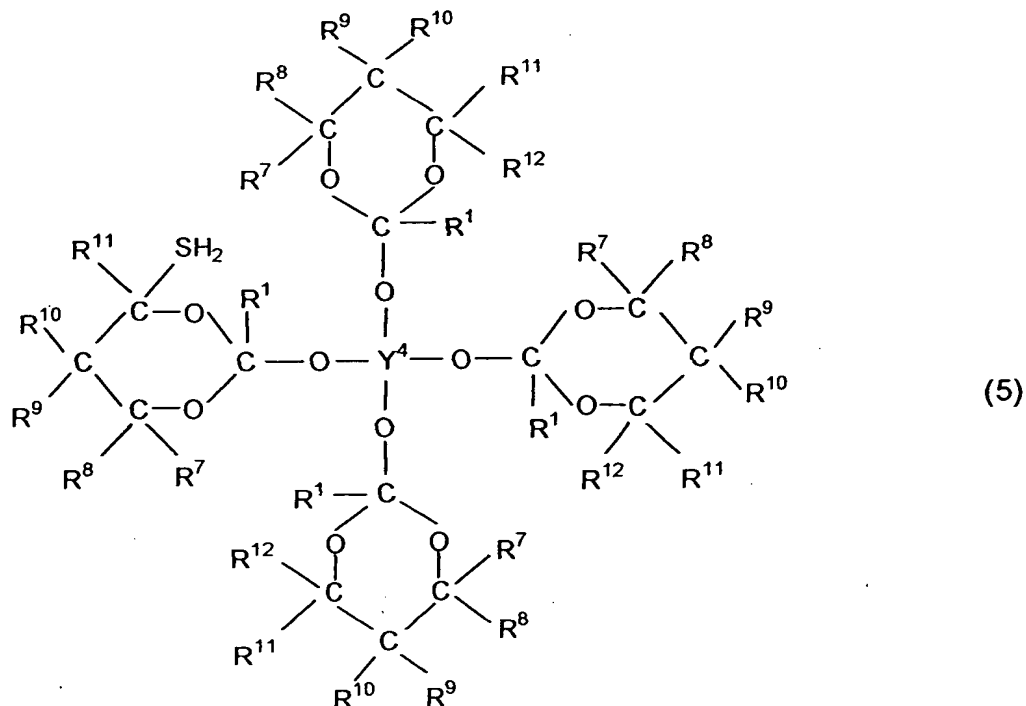
10 [0055]



[0056]

- wherein  $\text{Y}^1$  represents a residue obtained by removing 2 hydroxyl groups from the compound having 2 hydroxyl groups in a molecule; and  $\text{R}^1$ ,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  and  $\text{R}^6$  are the same as defined above. Also, when used as the raw materials are, for example, the orthoester represented by Formula (1) described above, the  $\beta$ -glycol represented by Formula (3) described above and the compound having 4 hydroxyl groups in a molecule, the polyorthoester of the present invention produced in the manner described above can have a structure represented by the following Formula (5):
- 15
- 20

[0057]



[0058]

wherein  $Y^2$  represents a residue obtained by removing the four hydroxyl groups  
 5 from the compound having four hydroxyl groups in a molecule; and  $R^1$ ,  $R^7$ ,  $R^8$ ,  
 $R^9$ ,  $R^{10}$ ,  $R^{11}$  and  $R^{12}$  are the same as defined above.

[0059]

The polyorthoester provided by the present invention can be used as  
 a binder, a cross-linking agent and a reactive diluent for coating materials, inks  
 10 and adhesives. Further, it can be used as a hydrolytic polymer, a  
 biodegradable polymer and a controlled release chemical.

[0060]

[Examples]

The present invention shall more specifically be explained below with  
 15 reference to examples and comparative examples, and "parts" and "%" mean  
 "parts by weight" and "% by weight" respectively.

[0061]

Production Example 1: Production of polyester solution

A reactor equipped with a stirrer, a condenser, a  
 20 temperature-controlling device, a water separator, a fractionating column, a

nitrogen-introducing tube and a solvent-recovering device was charged with 161 parts of 1,6-hexanediol, 351 parts of 1,4-dimethylolcyclohexane, 146 parts of trimethylolpropane, 114 parts of adipic acid, 300 parts of hexahydrophthalic anhydride and 243 parts of isophthalic acid, and the reactor was substituted  
 5 with nitrogen and then started to be heated. The temperature was elevated at a fixed rate from 170°C to 230°C in 3 hours while removing condensation water and then maintained at 230°C for one hour. Thereafter, 50 parts of xylene was added, and the reaction was further promoted for 3 hours while maintaining at 230°C and removing condensation water by means of the water separator.  
 10 Then, the reactor was cooled down, and 464 parts of xylene was added thereto to obtain a polyester solution (E-1) having a non-volatile matter content of about 69% and a Gardner viscosity (20°C) of X. The resulting resin (solid matter) had a resin acid value of 6.5 mg KOH/g, a hydroxyl group value of 120 mg KOH/g, a number average molecular weight of 1,800 and a weight average  
 15 molecular weight of 5,200.

[0062]

#### Production Example 2: Production of acrylic resin solution

A reactor equipped with a stirrer, a condenser, a  
 temperature-controlling device, a nitrogen-introducing tube and a dropping  
 20 funnel was charged with 983 parts of xylene and 240 parts of 3-methoxybutyl acetate, and the reactor was substituted with nitrogen, heated and maintained at 135°C. Added drop by drop thereto in 4 hours was a mixture comprising 600 parts of styrene, 636 parts of isobutyl methacrylate, 552 parts of  
 2-ethylhexyl acrylate, 612 parts of 2-hydroxyethyl methacrylate and 192 parts of  
 25 azobisisobutyronitrile. After finishing dropping, the solution was ripened at 135°C for 30 minutes, and then, a mixed solution comprising 168 parts of xylene and 12 parts of azobisisobutyronitrile was added drop by drop thereto in one hour. Then, the solution was maintained at 135°C for 30 minutes to obtain  
 an acrylic resin solution (A-1) having a non-volatile matter content of about 63%  
 30 and a Gardner viscosity (20°C) of U\*. The resulting resin (solid matter) had a hydroxyl group value of 110 mg KOH/g, a number average molecular weight of 1,900 and a weight average molecular weight of 4,300.

[0063]

### Example 1

A reactor equipped with a stirrer, a condenser, a temperature-controlling device and a solvent-recovering device was charged with 424 parts of methyl orthoformate, 640 parts of 2-butyl-2-ethyl-1,3-propanediol, 136 parts of pentaerythritol and 4 parts of a 90% formic acid aqueous solution and maintained at about 85°C for one hour while distilling off methanol produced by alcohol exchange reaction. Then, the temperature was elevated up to 190°C in 2 hours, and 365 parts of methanol was recovered to obtain a colorless and liquid polyorthoester. The polyorthoester thus obtained had a Gardner viscosity of X<sup>+</sup> and a weight average molecular weight of 1,540.

[0064]

### Examples 2 to 12 and Comparative Examples 1 to 3

The reaction was carried out in the same manner as in Example 1 to obtain the respective polyorthoesters, except that in Example 1, the blended raw material compositions were changed as shown in the following Table 1. In Examples 6 and 7, distilled off was a part of an organic solvent (xylene) contained in the raw material in addition to alcohol produced by alcohol exchange. The polyorthoester solution obtained in Example 6 had a solid content of about 74%, and the polyorthoester solution obtained in Example 7 had a solid content of about 68%.

[0065]

The polyorthoester obtained in Comparative Example 1 had a solid content of about 100% and crystallized. In Comparative Example 2 and Comparative Example 3, gelation took place in the middle of the reaction.

[0066]

All the polyorthoesters obtained in Examples 1 to 5 and 8 to 12 were colorless and liquid polyorthoesters and had a solid content of substantially about 100%. In Example 6 and Comparative Example 2, the acid catalyst was not blended, but a carboxyl group contained in the resin in the polyester solution (E-1) works as a catalyst.

[0067]

A remark in Table 1 means the following:

(Remark 1) Placel 305: polycaprolactonepolyol, manufactured by Daicel Chemical Industries, Ltd.

[0068]

[Table 1]

Table 1

	Example												Comparative Example		
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3
Component (A)	Methyl orthoformate	424				106			424	636	424	424	212	35	
	Ethyl orthoacetate				480		120	360							40
	Ethyl orthoformate		592												
	2-Butyl-2-ethyl-1,3-propanediol	640	640	640		160	160		320	160	640				
Component (B)	Neopentyl glycol			416				312							
	2,2,4-trimethyl-1,3-pentanediol				584										
	1,2-Hexanediol											472			

To be continued

Table 1 (continued)

	Example												Comparative Example			
	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	
Component (C)	Pentaerythritol	136	136	136	136	136			68	136	136	136	136			
	Polyester solution (E-1)					668								668		
	Acrylic resin solution (A-1)						850								850	
	Placel 305 (remark 1)							550								
	Trimethylol-propane								268	536						
Acid catalyst	90 % formic acid aqueous solution	4	4	4	4	4	2	3	8	6		4	4		2	
	p-Toluenesulfonic acid										1					
Recovered alcohol	Methanol	365		360	366	342	91	92	267	362	523	341	360	130	16	22
	Ethanol		539													
Properties of polyorthoester (solution)	Gardner viscosity	X <sup>+</sup>	W	M	G <sup>+</sup>	A1 <sup>+</sup>	Z	UV	S	OP	W	Y	T	Crystal-lized	Gelled	Gelled
	Weight average molecular weight	1540	1420	1060	430	410	6950	5620	1640	1250	1600	1590	1270	—	—	—



[0069]

A weight average molecular weight, a hydroxyl group value and a viscosity of the polyorthoesters obtained in Examples 1 and 11 were compared with those of Placel 303, and the results thereof are shown in the following

5 Table 2.

[0070]

A remark in Table 2 means the following:

(Remark 2) Placel 303: polycaprolactonepolyol, manufactured by Daicel Chemical Industries, Ltd.

10 [0071]

[Table 2]

Table 2

	Weight average molecular weight	Hydroxyl group value* (mg KOH/g)	Viscosity (mPa·s)
Polyorthoester of Production Example 1	1540	550	1350
Polyorthoester of Production Example 11	1590	550	1420
Pracel 303 (remark 2)	610	540	1800

15 \* The hydroxyl group value represents a hydroxyl group value obtained after hydrolysis (a hydroxyl group value after recovering a hydroxyl group) in polyorthoesters.

[0072]

20

It is apparent from the results shown in Table 1 that all the polyorthoesters obtained in Examples 2 to 5 and Examples 8 to 10 and 12 had a lower Gardner viscosity than that of the polyorthoester obtained in Example 1.

[0073]

25 The polyorthoester obtained in Example 6 had a solid content of about 74%, and when the solid content was controlled to 69% by adding xylene to the above polyorthoester, the Gardner viscosity was V, which was lower than

the viscosity X of the polyester solution (E-1) having a solid content of 69% used in Example 6.

[0074]

Further, the polyorthoester solution obtained in Example 7 had a  
5 solid content of about 68%, and when the solid content was controlled to 63% by adding xylene to the above polyorthoester, the Gardner viscosity was O, which was lower than the viscosity  $U^+$  of the polyester solution (E-1) having a solid content of 63% used as a raw material in Example 7.

[0075]

10 [Effect of the invention]

The polyorthoester of the present invention comprises an orthoester structure introduced into a hydroxyl group part of a hydroxyl group-containing compound and has a high degree of freedom in molecular design, and it can be applied to various fields and is industrially very useful. The polyorthoester of  
15 the present invention can be produced without causing gelation and a marked rise in a viscosity, and it has a low viscosity and can readily be controlled in a molecular weight.

[0076]

The polyorthoester of the present invention can be produced by  
20 means of the same apparatus as a conventional polyester resin production apparatus in which alcohol produced by condensation can be distilled off, and therefore, it does not require a specific apparatus and can readily be produced, so that it is industrially useful from such point of view.

[Document Name] Abstract

[Abstract]

[Subject]

The present invention provides a novel polyorthoester which has a high degree of freedom in molecular design and a low viscosity and is readily controlled in a molecular weight.

[Means for Solution]

A polyorthoester which is prepared by reacting (A) an orthoester such as methyl orthoformate, ethyl orthoformate, methyl orthoacetate or ethyl orthoacetate, (B) at least one glycol compound selected from  $\alpha$ -glycols and  $\beta$ -glycols, and (C) a hydroxyl group-containing compound having at least two hydroxyl groups in a molecule other than the compound (B) described above; and a production process for the polyorthoester characterized by subjecting the orthoester (A), the glycol compound (B) and the hydroxyl group-containing compound (C) to condensation reaction in the presence of an acid catalyst.

[Selected Drawing]

None